

Chemistry–A European Journal

Supporting Information

Synthesis of a Molecule with Five Different Adjacent Pnictogens

Christian Ritter,^[a] Florian Weigend,^[b] and Carsten von Hänisch^{*[a]}

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1 Solid State Structures

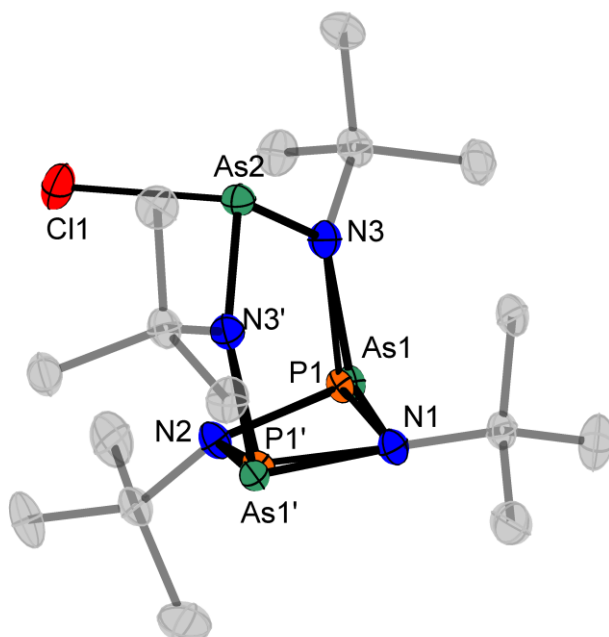


Figure S1. Molecular structure of $[\text{As}_{1.09}\text{P}_{0.91}(\text{NtBu})_2](\text{tBuN})_2\text{AsCl}$ in the solid state. Ratio of P/As occupancy $\approx 0.45/0.55$. Carbon atoms are shaded and hydrogen atoms are omitted for clarity. Displacement ellipsoids represent a 50 % probability level at 100 K.

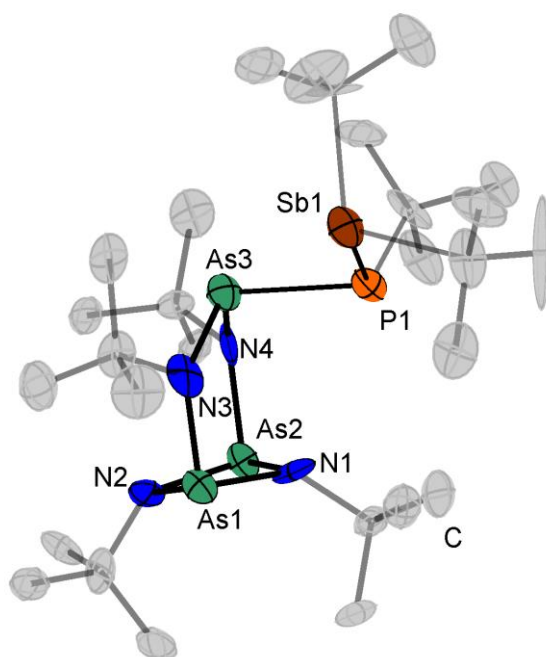


Figure S2. Molecular Structure of **5** in the solid state Carbon atoms are shaded and hydrogen atoms are omitted for clarity. Displacement ellipsoids represent a 50 % probability level at 100 K.

2 Experimental

All manipulations were performed under an inert argon atmosphere using standard Schlenk techniques. The solvents were dried by standard procedures and freshly distilled before being used.^[1] The storage and use of moisture or air sensitive substances are carried out under an inert argon atmosphere in a glovebox. $(t\text{Bu}_2\text{SbP}[\text{Li}\cdot\text{OEt}_2]t\text{Bu})_2$ ^[2] $(t\text{BuNAs})_2(t\text{BuNH})_2$ ^[3] were prepared according to literature methods. AsCl_3 and BiCl_3 were purchased from Sigma Aldrich, $n\text{BuLi}$ solution from Acros Organics and SbCl_3 from Alfa Aesar. SbCl_3 and BiCl_3 were purified by sublimation prior to use. NMR spectra were recorded at 300 K on a Bruker AV II 300, AV III HD 300 and AV III 500. The coupling constants J were reported in Hertz (Hz) and the chemical shift (δ) is given in ppm relative to the standard (^{31}P : H_3PO_4 ; ^1H , ^{13}C : SiMe_4). IR spectra were recorded on a Bruker ALPHA FT-IR with a diamond ATR (400–4000 cm^{-1}). Mass spectrometry was performed either on a Jeol AccuTOF GCv (LIFDI, CI). The microanalyses were done with elemental vario MICRO cube instrument. The UV/Vis spectrum was recorded on an analytikjena Specord S 600 single beam photometer at room temperature.

$[(t\text{BuNAs})_2(t\text{BuNLi})_2]_2$ (**1₂**)

$(t\text{BuNAs})_2(t\text{BuNH})_2$ (2.14 g, 4.91 mmol, 1.00 eq.) was dissolved in *n*pentane (70 mL) and cooled to -80°C . Slow addition of a solution of $n\text{BuLi}$ in *n*hexane (2.5M, 3.73 mL, 9.32 mmol, 1.90 eq.) leads to a slightly yellow solution. Afterwards, the reaction mixture was allowed to warm to room temperature and the solvent was evaporated *in vacuo*. After drying of the crude product it can be recrystallized from *n*pentane (15.0 mL) to yield **1₂** as a colourless crystalline solid (1.73 g, 1.93 mmol, 79%).

^1H NMR (300 MHz, C_6D_6): δ = 1.24 (s, 18H, As_2NtBu), 1.32 (s, 18H, AsNtBuLi) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): δ = 31.0 (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 37.9 (s, $\text{N}(\text{Li})\text{C}(\text{CH}_3)_3$), 53.9 (s, $\text{As}_2\text{NC}(\text{Me})_3$), 54.4 (s, $\text{N}(\text{Li})\text{C}(\text{Me})_3$) ppm.

^7Li NMR (117 MHz, C_6D_6): δ = -2.13 ppm.

Elemental Analysis: (Found) C: 42.73, H: 7.93, N: 12.76; (calc.) C: 42.88, H: 8.10, N: 12.50.

IR: ν =2954 (m), 2858 (w), 1475 (w), 1462 (w), 1376 (w), 1357 (m), 1174 (s), 1025 (w), 917 (m), 905 (s), 767 (m), 718 (s), 687 (s), 665 (s), 545 (m), 482 (w), 469 (w), 412 (w) cm^{-1} .

$[(t\text{BuNAs})_2(t\text{BuN})_2\text{AsCl}]$ (**2**)

1 (0.48 g, 1.06 mmol, 1.00 eq.) was dissolved in DME (10.0 mL) and cooled to -60°C . Then AsCl_3 (0.19 g, 1.06 mmol, 1.00 eq.) dissolved in DME (10.0 mL) was added slowly. The solution initially turns intensively yellow but gets decolourized after the addition is complete. Afterwards, the reaction mixture was allowed to warm to room temperature and the solvent was evaporated *in vacuo*. The crude product was dissolved in toluene (20.0 mL) and filtered through a D4 frit. Concentration of the solution to 10 mL and cooling to -32°C yields **2** as a pale yellow crystalline solid (0.36 g, 0.67 mmol, 62%).

^1H NMR (300 MHz, C_6D_6): δ = 1.24 (s, 9H, As_2NtBu), 1.46 (s, 27H, ClAsNtBu & As_2NtBu) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): δ = 30.6 (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 32.5 (s, $\text{ClAsNC}(\text{CH}_3)_3$), 54.1 (s, $\text{As}_2\text{NC}(\text{Me})_3$), 54.9 (s, $\text{As}_2\text{NC}(\text{Me})_3$), 59.7 (s, $\text{ClAsNC}(\text{Me})_3$) ppm.

HR-MS: $\text{Cl}(+)$ m/z = 544.02603 $[\text{M}]^+$; cal. = 544.02764.

Elemental Analysis: (Found) C: 35.80, H: 6.65, N: 10.39; (calc.) C: 35.28, H: 6.66, N: 10.29.

IR: ν = 2954 (m), 2862 (w), 1464 (m), 1387 (w), 1359 (m), 1237 (w), 1203 (m), 1177 (s), 1038 (w), 980 (m), 925 (m), 906 (m), 810 (s), 710 (w), 515 (w), 485 (w), 462 (w), 419 (m) cm^{-1} .

$[(t\text{BuNAs})_2(t\text{BuN})_2\text{SbCl}]$ (3**)**^[4]

1 (0.31 g, 0.69 mmol, 1.00 eq.) was dissolved in DME (10.0 mL) and cooled to -60°C . Then SbCl_3 (0.16 g, 0.69 mmol, 1.00 eq.) dissolved in DME (10.0 mL) was added slowly. The solution initially turns pale yellow but gets decolourized after the addition is complete. Afterwards, the reaction mixture was allowed to warm to room temperature and the solvent was evaporated *in vacuo*. The crude product was dissolved in toluene (20.0 mL) and filtered through a D4 frit. Concentration of the solution to 8.00 mL and cooling to -32°C yields **3** as a colourless crystalline solid (0.39 g, 0.66 mmol, 95%).

^1H NMR (300 MHz, C_6D_6): δ = 1.10 (s, 9H, As_2NtBu), 1.31 (s, 9H, As_2NtBu), 1.64 (s, 18H, SbNtBu) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): δ = 25.9 (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 32.4 (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 35.0 (s, $\text{SbNC}(\text{CH}_3)_3$), 54.7 (s, $\text{As}_2\text{NC}(\text{Me})_3$), 55.3 (s, $\text{As}_2\text{NC}(\text{Me})_3$), 59.3 (s, $\text{SbNC}(\text{Me})_3$) ppm.

HR-MS: $\text{Cl}(+)$ m/z = 592.01034 $[\text{M}]^+$; cal. = 592.01026.

IR: ν = 2956 (m), 2945 (m), 2857 (w), 1458 (w), 1387 (w), 1359 (s), 1182 (s), 1033 (w), 968 (m), 939 (m), 789 (s), 774 (s), 750 (s), 727 (s), 598 (m), 516 (w), 495 (s), 480 (w), 413 (w) cm^{-1} .

$[(t\text{BuNAs})_2(t\text{BuN})_2\text{BiCl}]$ (4**)**^[4]

1 (0.31 g, 0.69 mmol, 1.00 eq.) was dissolved in DME (10.0 mL) and cooled to -60°C . Then BiCl_3 (0.22 g, 0.69 mmol, 1.00 eq.) dissolved in DME (10.0 mL) was added slowly. Upon addition the solution turns intensively yellow. Then, the reaction mixture was allowed to warm to room temperature and the solvent was evaporated *in vacuo*. The crude product was dissolved in toluene (20.0 mL) and filtered through a D4 frit. Concentration of the solution to 8.00 mL and cooling to -32°C yields **4** as a yellow crystalline solid (0.44 g, 0.64 mmol, 93%).

^1H NMR (300 MHz, C_6D_6): δ = 1.18 (s, 18H, As_2NtBu), 1.51 (s, 18H, BiNtBu) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): δ = 29.7 (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 36.4 (s, $\text{BiNC}(\text{CH}_3)_3$), 54.8 (s, $\text{As}_2\text{NC}(\text{Me})_3$), 58.6 (s, $\text{BiNC}(\text{Me})_3$) ppm.

HR-MS: $\text{Cl}(+)$ m/z = 678.08387 $[\text{M}]^+$; cal. = 678.08643.

Elemental Analysis: (Found) C: 28.15, H: 5.28, N: 8.23; (calc.) C: 28.31, H: 5.35, N: 8.25.

IR: ν = 2952 (m), 2896 (w), 2858 (w), 1458 (w), 1385 (w), 1356 (m), 1262 (w), 1183 (s), 1098 (w), 1032 (w), 972 (m), 940 (m), 788 (m), 770 (m), 728 (s), 589 (m), 522 (w), 504 (w), 490 (w), 472 (w), 410 (w) cm^{-1} .

$[(t\text{BuNAs})_2(t\text{BuN})_2\text{AsP}(t\text{Bu})\text{SbtBu}_2]$ (5**)**

2 (0.13 g, 0.23 mmol, 2.00 eq.) was dissolved in Et_2O (10.0 mL), cooled to -40°C and $(t\text{Bu}_2\text{SbP}[\text{Li}\cdot\text{OEt}_2]t\text{Bu})_2$ (92.0 mg, 0.11 mmol, 1.00 eq.) dissolved in Et_2O (10.0 mL) was added slowly. Upon addition the solution turns yellow. Then, the reaction mixture was allowed to warm to room

temperature and the solvent was evaporated *in vacuo*. After drying in a fine vacuum the crude product was dissolved in *n*pentane (10.0 mL) and filtered through a D4 frit. Concentration of the solution to 1.00 mL and cooling to $-32\text{ }^{\circ}\text{C}$ yields a mixture of compounds containing **5** as a yellow crystals.

$^{31}\text{P}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): $\delta = 61.7$ (s, As(Sb)PtBu) ppm.

^{31}P NMR (101 MHz, C_6D_6): $\delta = 61.7$ (m, As(Sb)PtBu) ppm.

$[(\text{tBuNAS})_2(\text{tBuN})_2\text{SbP}(\text{tBu})\text{Sb}(\text{tBu})_2]$ (6**)**

3 (0.13 g, 0.21 mmol 2.00 eq.) was dissolved in Et_2O (10.0mL), cooled to $-40\text{ }^{\circ}\text{C}$ and $(\text{tBu}_2\text{SbP}[\text{Li}\cdot\text{OEt}_2]\text{tBu})_2$ (86.0 mg, 0.11 mmol, 1.00 eq.) dissolved in Et_2O (10.0 mL) was added slowly. Upon addition the solution turns yellow. Then, the reaction mixture was allowed to warm to room temperature and the solvent was evaporated *in vacuo*. After drying in a fine vacuum the crude product was dissolved in *n*pentane (10.0 mL) and filtered through a D4 frit. Concentration of the solution to 1.00 mL and cooling to $-32\text{ }^{\circ}\text{C}$ yields **6** as a yellow crystalline solid (0.11 g, 0.13 mmol, 62 %).

^1H NMR (300 MHz, C_6D_6): $\delta = 1.29$ (s, 9H, As_2NtBu), 1.54 (s, 9H, As_2NtBu), 1.59 (s, 18H, $\text{Sb}(\text{tBu})_2$), 1.68 (s, 18H, $\text{Sb}(\text{As})\text{NtBu}$), 1.77 (d, $^3J_{\text{PH}} = 11.71$ Hz, 9H, PtBu) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta = 30.4$ (d, $^4J_{\text{CP}} = 5.0$ Hz, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 31.8 (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 32.9 (d, $^2J_{\text{CP}} = 4.6$ Hz, $\text{SbC}(\text{Me})_3$), 34.4 (d, $^3J_{\text{CP}} = 2.0$ Hz, $\text{SbC}(\text{CH}_3)_3$), 35.7 (d, $^4J_{\text{CP}} = 2.8$ Hz, $\text{SbNC}(\text{CH}_3)_3$), 36.4 (d, $^2J_{\text{CP}} = 11.8$ Hz, $\text{PC}(\text{CH}_3)_3$), 39.0 (d, $^1J_{\text{CP}} = 52.2$ Hz, $\text{PC}(\text{CH}_3)_3$), 54.9 (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 55.7 (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 59.1 (s, $\text{SbNC}(\text{CH}_3)_3$) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): $\delta = 22.5$ (s, Sb(Sb)PtBu) ppm.

^{31}P NMR (101 MHz, C_6D_6): $\delta = 22.5$ (m, Sb(Sb)PtBu) ppm.

HR-MS: LIFDI(+) $m/z = 555.04370$ $[\text{M}-\text{tBuPSb}(\text{tBu})_2]^+$, cal.= 555.04101; 323.09032 $[\text{tBuPSb}(\text{tBu})_2]^+$, cal.= 323.08886.

Elemental Analysis: (Found) C: 37.67, H: 6.70, N: 6.73; (calc.) C: 38.21, H: 7.21, N: 6.37.

IR: $\nu = 2959$ (m), 2923 (w), 2887 (w), 2848 (w), 1459 (w), 1385 (w), 1359 (m), 1260 (s), 1180 (w), 1148 (w), 1093 (s), 1018 (s), 921 (w), 863 (w), 799 (s), 754 (w), 694 (w) cm^{-1} .

$[(\text{tBuNAS})_2(\text{tBuN})_2\text{BiP}(\text{tBu})\text{Sb}(\text{tBu})_2]$ (7**)**

4 (0.25 g, 0.37 mmol 2.00 eq.) was dissolved in Et_2O (10.0mL), cooled to $-40\text{ }^{\circ}\text{C}$ and $(\text{tBu}_2\text{SbP}[\text{Li}\cdot\text{OEt}_2]\text{tBu})_2$ (0.15 g, 0.19 mmol, 1.00 eq.) dissolved in Et_2O (7.5 mL) was added slowly. Upon addition the solution turns intensively red. Then, the reaction mixture was allowed to warm to room temperature and the solvent was evaporated *in vacuo*. The crude product was dissolved in *n*pentane (10.0 mL) and filtered through a D4 frit. Concentration of the solution to 1.00 mL and cooling to $-32\text{ }^{\circ}\text{C}$ yields **7** as a red crystalline solid (0.18 g, 0.19 mmol, 51 %).

^1H NMR (300 MHz, C_6D_6): $\delta = 1.30$ (s, 18H, As_2NtBu), 1.56 (s, 18H, $\text{Bi}(\text{As})\text{NtBu}$), 1.59 (s, 18H, $\text{Sb}(\text{tBu})_2$), 2.01 (d, $^3J_{\text{PH}} = 11.98$ Hz, 9H, PtBu) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta = 31.0$ (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 31.2 (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 33.7 (d, $^2J_{\text{CP}} = 5.2$ Hz, $\text{SbC}(\text{Me})_3$), 34.4 (d, $^3J_{\text{CP}} = 2.1$ Hz, $\text{SbC}(\text{CH}_3)_3$), 37.7 (d, $^4J_{\text{CP}} = 5.3$ Hz, $\text{BiNC}(\text{CH}_3)_3$), 38.7 (d, $^2J_{\text{CP}} = 50.2$ Hz,

$\text{PC}(\text{CH}_3)_3$, 39.6 (d, $^1J_{\text{CP}} = 11.4$ Hz, $\text{PC}(\text{CH}_3)_3$), 54.9 (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 55.0 (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 55.4 (s, $\text{As}_2\text{NC}(\text{CH}_3)_3$), 59.2 (s, $\text{BiNC}(\text{CH}_3)_3$) ppm.

$^{31}\text{P}\{\text{H}\}$ NMR (101 MHz, C_6D_6): $\delta = 37.6$ (s, $\text{Bi}(\text{Sb})\text{PtBu}$) ppm.

^{31}P NMR (101 MHz, C_6D_6): $\delta = 37.6$ (m, $\text{Bi}(\text{Sb})\text{PtBu}$) ppm.

HR-MS: $\text{Cl}(-)$ $m/z = 643.11975$ [M-tBuPSbtBu_2] $^-$, cal.= 643.11757; 323.08859 [tBuPSbtBu_2] $^-$, cal.= 323.08886.

Elemental Analysis: (Found) C: 34.51, H: 6.46, N: 5.51; (calc.) C: 34.76, H: 6.56, N: 5.79.

IR: $\nu = 2950$ (m), 2919 (m), 2883 (m), 2845 (m), 1455 (m), 1384 (m), 1356 (s), 1213 (m), 1177 (s), 1146 (m), 1029 (w), 950 (m), 915 (w), 784 (m), 758 (m), 716 (s), 515 (w), 480 (w), 408 (w) cm^{-1} .

3 X-ray Structure Analysis

The data were collected on a STOE IPDS 2 or STOE IPDS 2T diffractometer. The radiation used was monochromatic Mo-K α . The solution of the structure was performed with intrinsic phasing with the SHELXT-2015 solution program while for the structure refinement with full-matrix least-squares against F^2 the SHELXL-2015 package was used, both within the OLEX² environment.^[5–7]

Crystal Data of **1₂**:

C₃₂H₇₂As₄Li₄N₈, 896.41 g mol⁻¹, $T = 100$ K, monoclinic, $C2/c$, $a = 23.964(1)$ Å, $b = 9.7412(5)$ Å, $c = 24.158(1)$ Å, $\beta = 131.130(3)$, $V = 4247.6(4)$ Å³, $Z = 4$, $\rho = 1.402$ g cm⁻³, $\mu = 3.151$ mm⁻¹, $F(000) = 1856$, GooF = 1.036. A total of 12220 reflections was collected, of which 4165 were unique ($R(\text{int}) = 0.0361$). R_1 (wR_2 all data) = 0.0326 (0.0758) for 229 parameters and 3390 reflections ($I > 2\sigma(I)$). CCDC 1983180.

Crystal Data of **1·DME**:

C₂₀H₄₆As₂Li₂N₄O₂, 538.33 g mol⁻¹, $T = 100$ K, monoclinic, $P2_1/n$, $a = 9.9039(5)$ Å, $b = 18.8433(6)$ Å, $c = 15.3740(7)$ Å, $\beta = 90.020(4)$, $V = 2869.1(2)$ Å³, $Z = 4$, $\rho = 1.246$ g cm⁻³, $\mu = 2.349$ mm⁻¹, $F(000) = 1128$, GooF = 1.289. A total of 29778 reflections was collected, of which 7275 were unique ($R(\text{int}) = 0.0290$). R_1 (wR_2 all data) = 0.0695 (0.1753) for 385 parameters and 6354 reflections ($I > 2\sigma(I)$). CCDC 1983179.

Crystal Data of **2**:

C₁₆H₃₆As₃ClN₄, 544.70 g mol⁻¹, $T = 100$ K, monoclinic, $P2_1/m$, $a = 9.778(2)$ Å, $b = 11.712(2)$ Å, $c = 9.986(2)$ Å, $\beta = 97.792(16)$, $V = 1133.0(4)$ Å³, $Z = 2$, $\rho = 1.597$ g cm⁻³, $\mu = 4.523$ mm⁻¹, $F(000) = 552$, GooF = 1.079. A total of 7619 reflections was collected, of which 2332 were unique ($R(\text{int}) = 0.0294$). R_1 (wR_2 all data) = 0.0290 (0.0744) for 126 parameters and 2104 reflections ($I > 2\sigma(I)$). CCDC 1983177.

Crystal Data of **4 · 1/2 toluene**:

C₃₉H₈₀As₄Bi₂Cl₂N₈, 1449.65 g mol⁻¹, $T = 100$ K, triclinic, $P\bar{1}$, $a = 9.5377(5)$ Å, $b = 11.9645(7)$ Å, $c = 13.1596(8)$ Å, $\alpha = 111.668(4)$, $\beta = 108.299(4)$, $\gamma = 90.013(4)$, $V = 1313.5(1)$ Å³, $Z = 1$, $\rho = 1.833$ g cm⁻³, $\mu = 9.326$ mm⁻¹, $F(000) = 702$, GooF = 1.056. A total of 41070 reflections was collected, of which 17736 were unique ($R(\text{int}) = 0.0272$). R_1 (wR_2 all data) = 0.0537 (0.1491) for 245 parameters and 16549 reflections ($I > 2\sigma(I)$). CCDC 1983182.

Crystal Data of **[(tBuNAs)₂(tBuN)₂AsP(tBu)SbtBu₂] (5)**:

C₂₈H₆₃As₃N₄PSb, 833.34 g mol⁻¹, $T = 100$ K, Mo-K α radiation, monoclinic, Cc , $a = 25.558(2)$ Å, $b = 14.669(1)$ Å, $c = 21.036(2)$ Å, $\beta = 109.241(5)^\circ$, $V = 7446(1)$ Å³, $Z = 8$, $\rho = 1.487$ g cm⁻³, $\mu = 3.452$ mm⁻¹, $F(000) = 3392$, GooF = 0.985. A total of 23776 reflections was collected, of which 13230 were unique ($R(\text{int}) = 0.0955$). R_1 (wR_2 all data) = 0.0890 (0.2211) for 650 parameters and 7986 reflections ($I > 2\sigma(I)$). Flack parameter = -0.008(5). CCDC 1983178.

Crystal Data of 6:

$C_{28}H_{63}As_2N_4PSb_2$, 880.13 g mol⁻¹, $T = 100$ K, Mo-K α radiation, monoclinic, Cc , $a = 25.216(5)$ Å, $b = 14.794(3)$ Å, $c = 21.240(4)$ Å, $\beta = 108.31(3)^\circ$, $V = 7522(3)$ Å³, $Z = 8$, $\rho = 1.554$ g cm⁻³, $\mu = 3.247$ mm⁻¹, $F(000) = 3536$, GooF = 1.000. A total of 49008 reflections was collected, of which 14632 were unique ($R(int) = 0.0230$). R_1 (wR_2 all data) = 0.0240 (0.0538) for 709 parameters and 13510 reflections ($I > 2\sigma(I)$). Flack parameter = -0.014(6). CCDC 1983184.

Crystal Data of 7:

$C_{28}H_{63}As_2BiN_4PSb$, 967.36 g mol⁻¹, $T = 100$ K, triclinic, $P\bar{1}$, $a = 9.9436(7)$ Å, $b = 13.3807(8)$ Å, $c = 15.7597(11)$ Å, $\alpha = 100.892(5)^\circ$, $\beta = 105.489(6)^\circ$, $\gamma = 103.984(5)^\circ$, $V = 1887.4(2)$ Å³, $Z = 2$, $\rho = 1.702$ g cm⁻³, $\mu = 7.175$ mm⁻¹, $F(000) = 948$, GooF = 0.954. A total of 33940 reflections was collected, of which 7401 were unique ($R(int) = 0.0446$). R_1 (wR_2 all data) = 0.0455 (0.1121) for 355 parameters and 5331 reflections ($I > 2\sigma(I)$). CCDC 1983183.

Crystal Data of [As_{1.09}(NtBu)₂P_{0.91}](tBuN)₂AsCl:

$C_{16}H_{36}As_{2.09}ClN_4P_{0.91}$, 504.48 g mol⁻¹, $T = 100$ K, monoclinic, $P2_1/m$, $a = 9.716(2)$ Å, $b = 11.744(2)$ Å, $c = 9.935(2)$ Å, $\beta = 97.89(3)$, $V = 1123.0(4)$ Å³, $Z = 2$, $\rho = 1.506$ g cm⁻³, $\mu = 3.291$ mm⁻¹, $F(000) = 528$, GooF = 1.097. A total of 8050 reflections was collected, of which 2316 were unique ($R(int) = 0.0202$). R_1 (wR_2 all data) = 0.0230 (0.0576) for 136 parameters and 2084 reflections ($I > 2\sigma(I)$). CCDC 1983181.

4 UV-Vis Spectra, measured and calculated

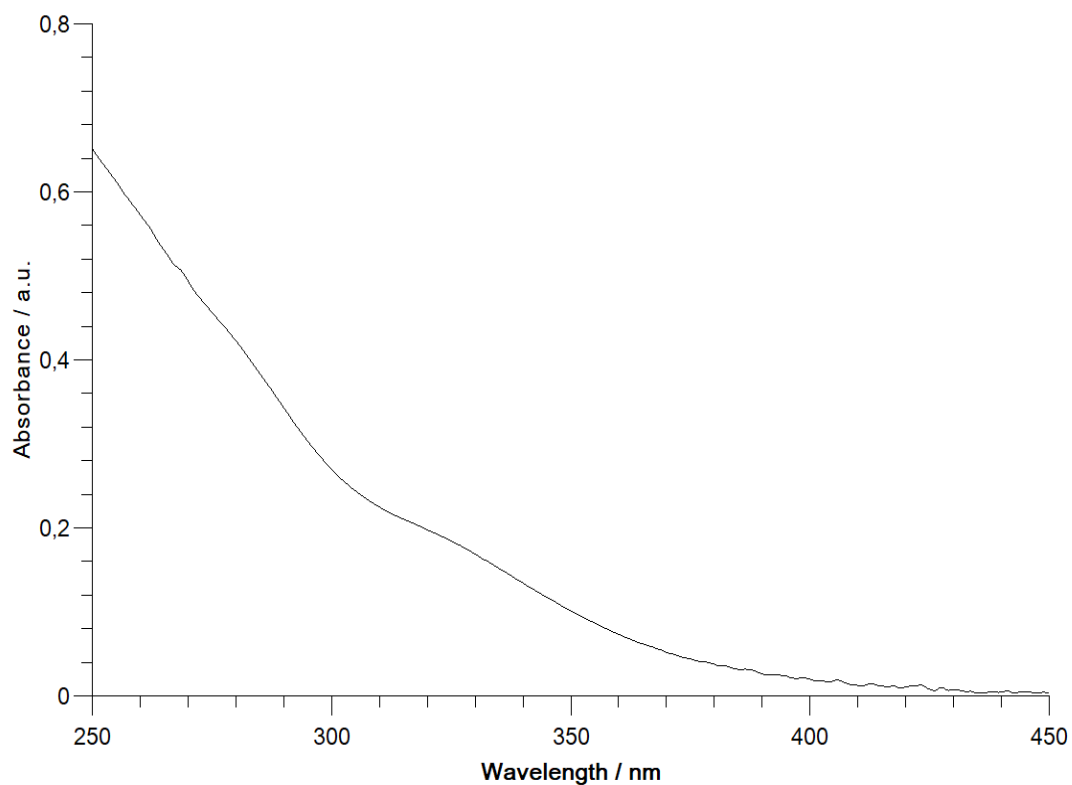


Figure S3. UV-Vis-Spectra of **6** in *n*heptane.

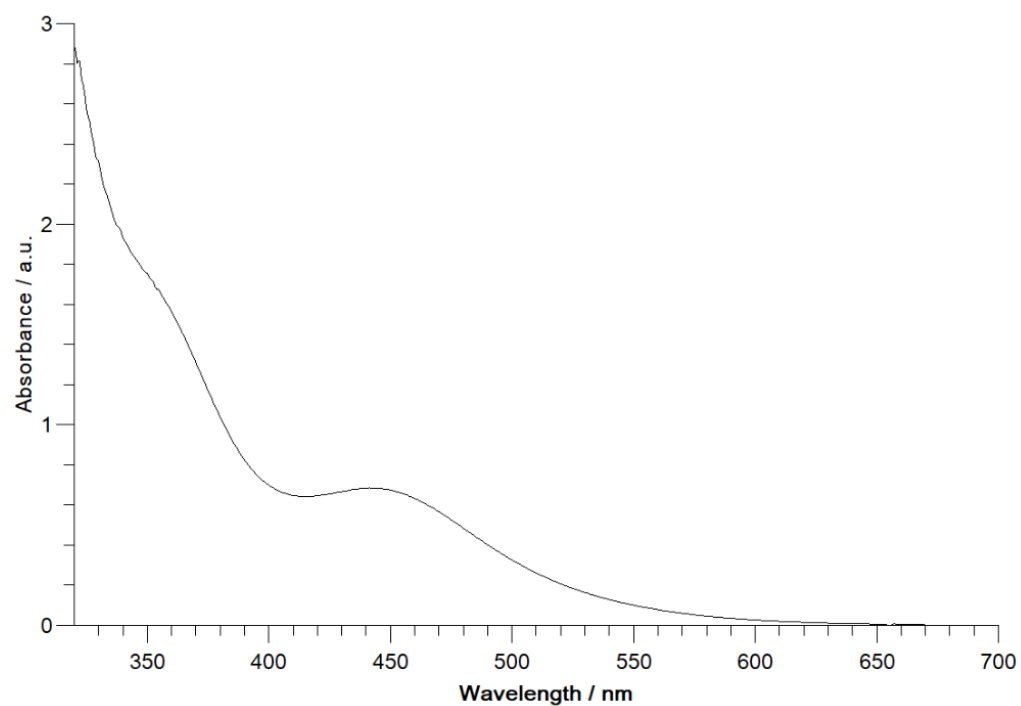


Figure S4. UV-Vis-Spectra of **7** in toluene.

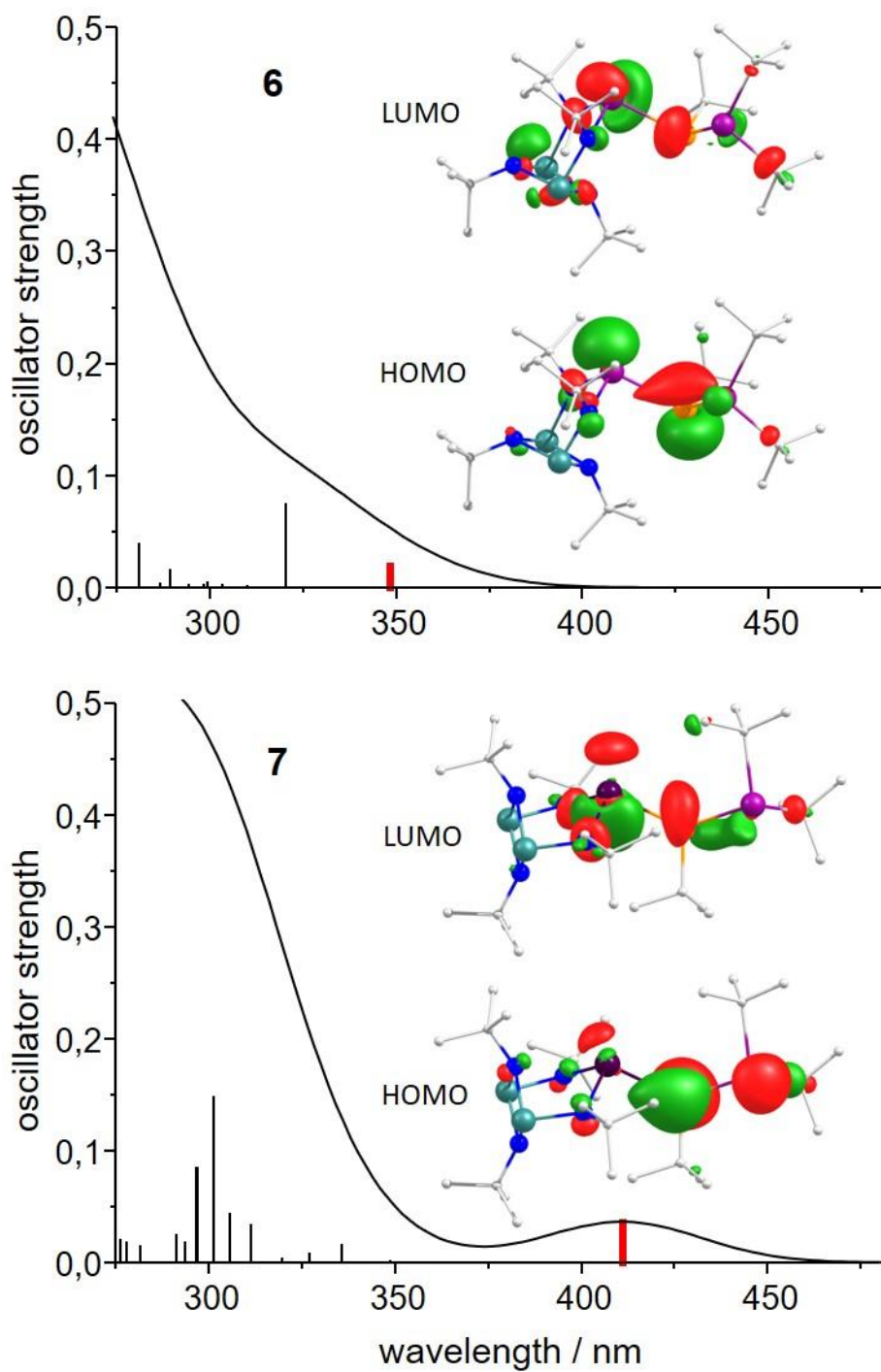


Figure S5. Calculated excitation energies and simulated spectra (FWHM = 50 nm) for compounds **6** and **7**. The first excitation peak is marked in red. In both cases it is a transition from the HOMO to the LUMO, which are plotted with iso-surfaces drawn at 0.05 a.u. For details concerning the DFT calculations, see main text.

5 Mass Spectra

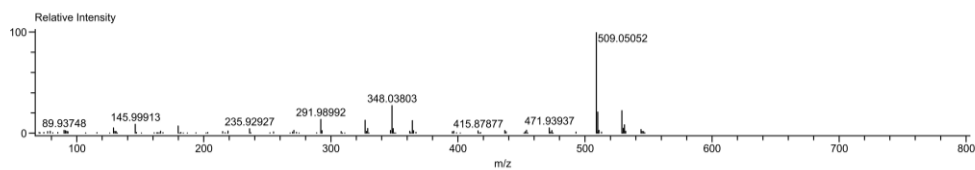


Figure S6. CI(+)-MS of **2**.

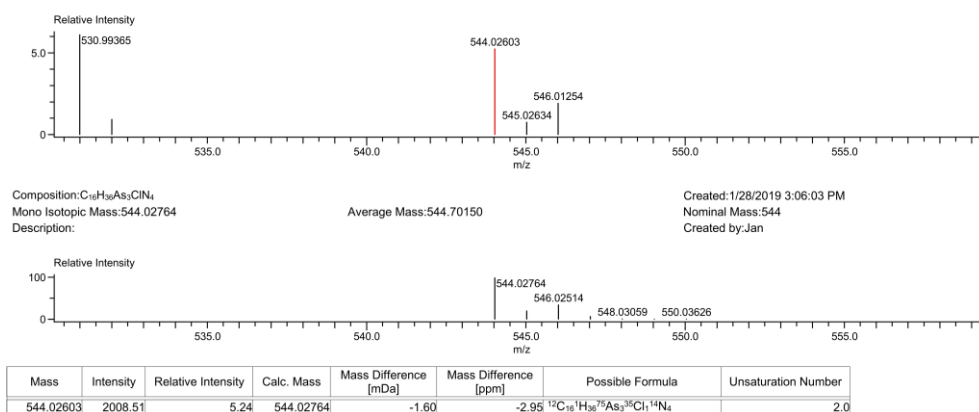


Figure S7. HR-Cl(+)-MS of **2** as [M]⁺ (top) and simulation of the corresponding sum formula (bottom).

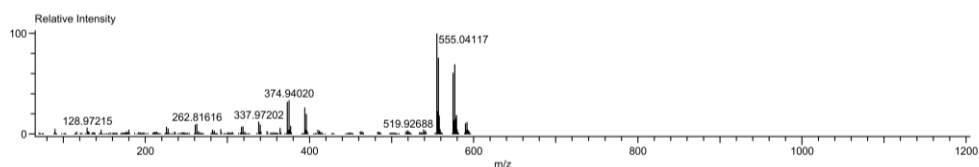


Figure S8. CI(+)-MS of **3**.

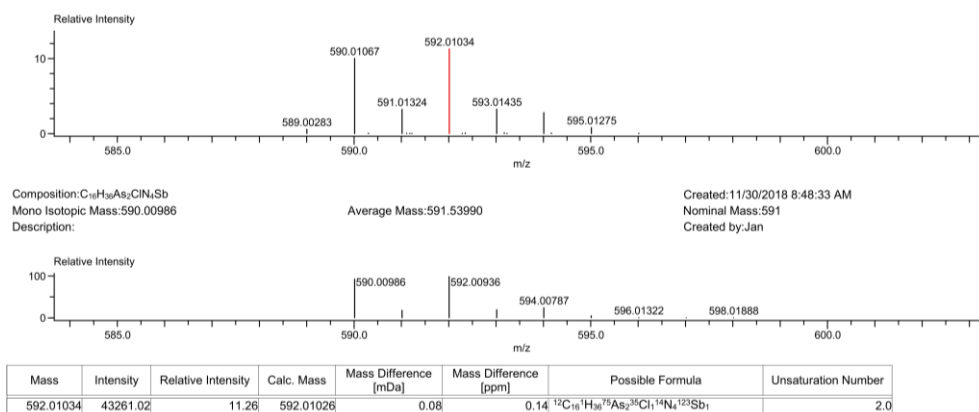


Figure S9. HR-Cl(+)-MS of **3** as [M]⁺ (top) and simulation of the corresponding sum formula (bottom).

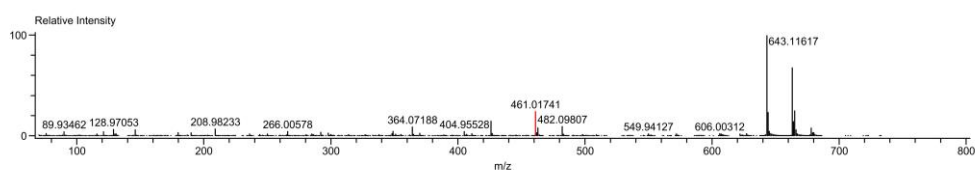


Figure S10. CI(+)-MS of **4**.

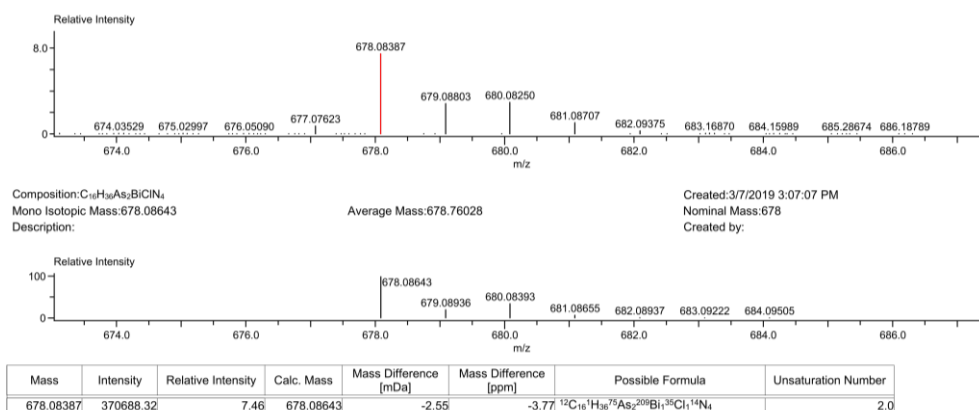


Figure S11. HR-Cl(+)-MS of **4** as $[M]^+$ (top) and simulation of the corresponding sum formula (bottom).

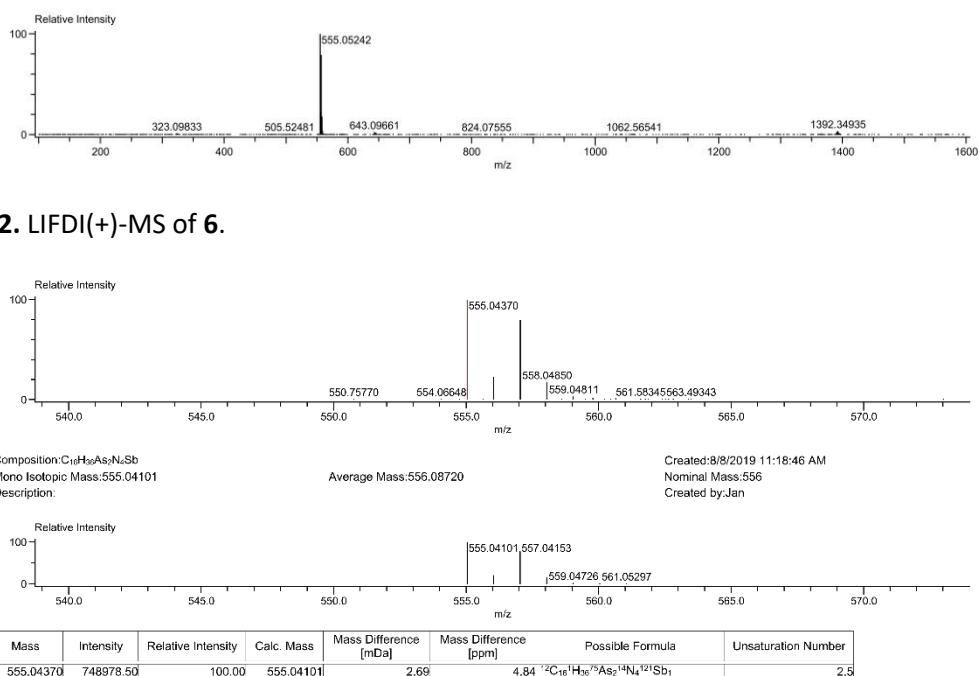


Figure S13. HR-LIFDI(+)-MS of **6** as $[M-tBuPSbtBu_2]^+$ (top) and simulation of the corresponding sum formula (bottom).

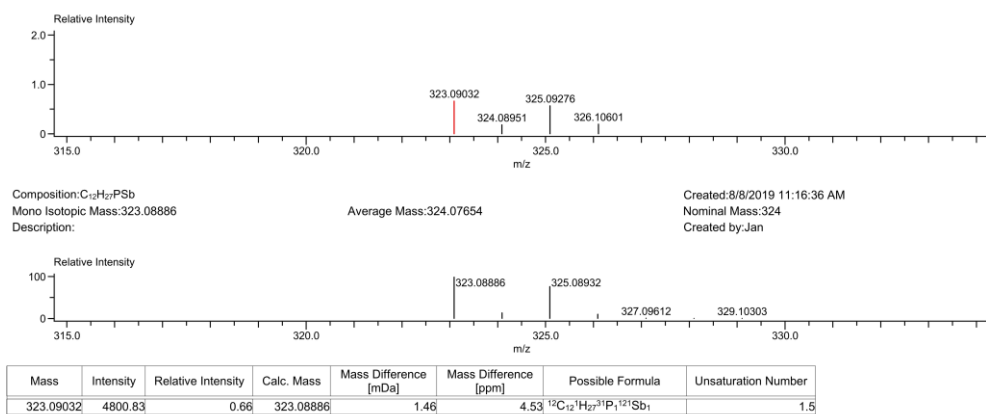


Figure S14. HR-LIFDI(+)-MS of [tBuPSbtBu₂]⁺ (top) and simulation of the corresponding sum formula (bottom).

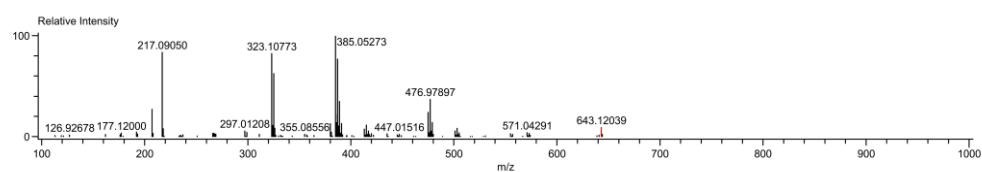


Figure S15. CI(-)-MS of **7**.

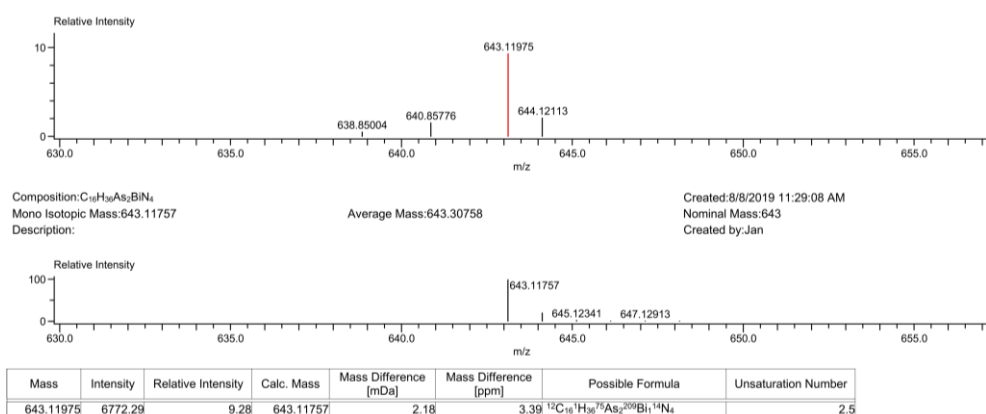


Figure S16. HR-CI(-)-MS of **7** as [M-tBuPSbtBu₂]⁻ (top) and simulation of the corresponding sum formula (bottom).

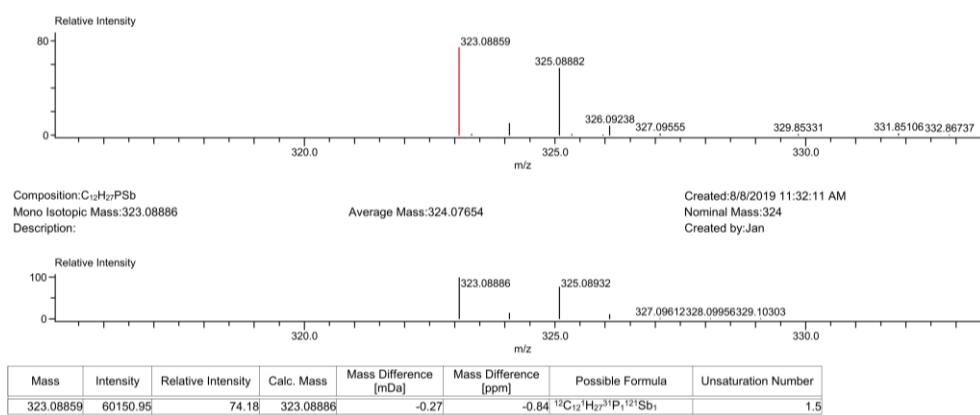


Figure S17. HR-Cl(-)-MS of [tBuPSbtBu₂]⁻ (top) and simulation of the corresponding sum formula (bottom).

6 NMR Spectra

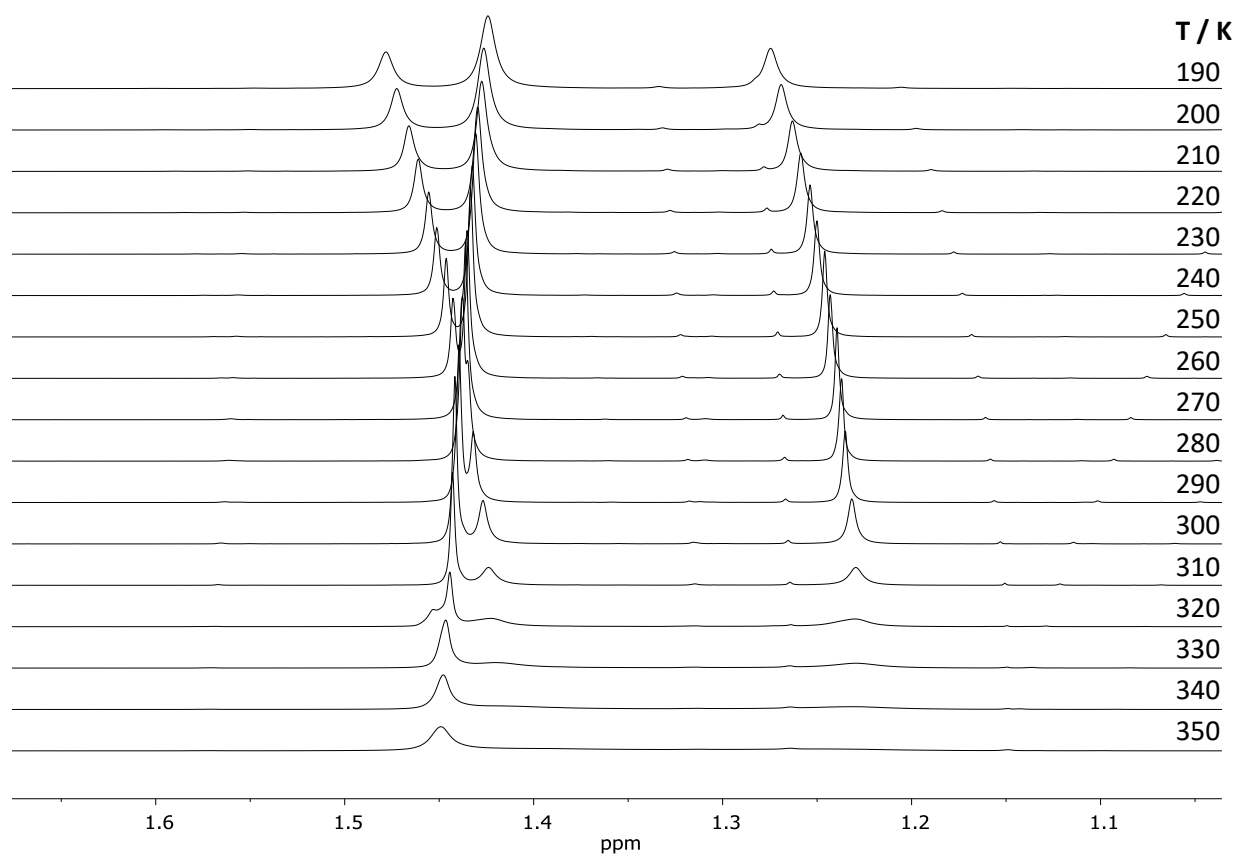


Figure S18. VT-¹H NMR spectrum of **2** (500 MHz, toluene-*d*⁸).

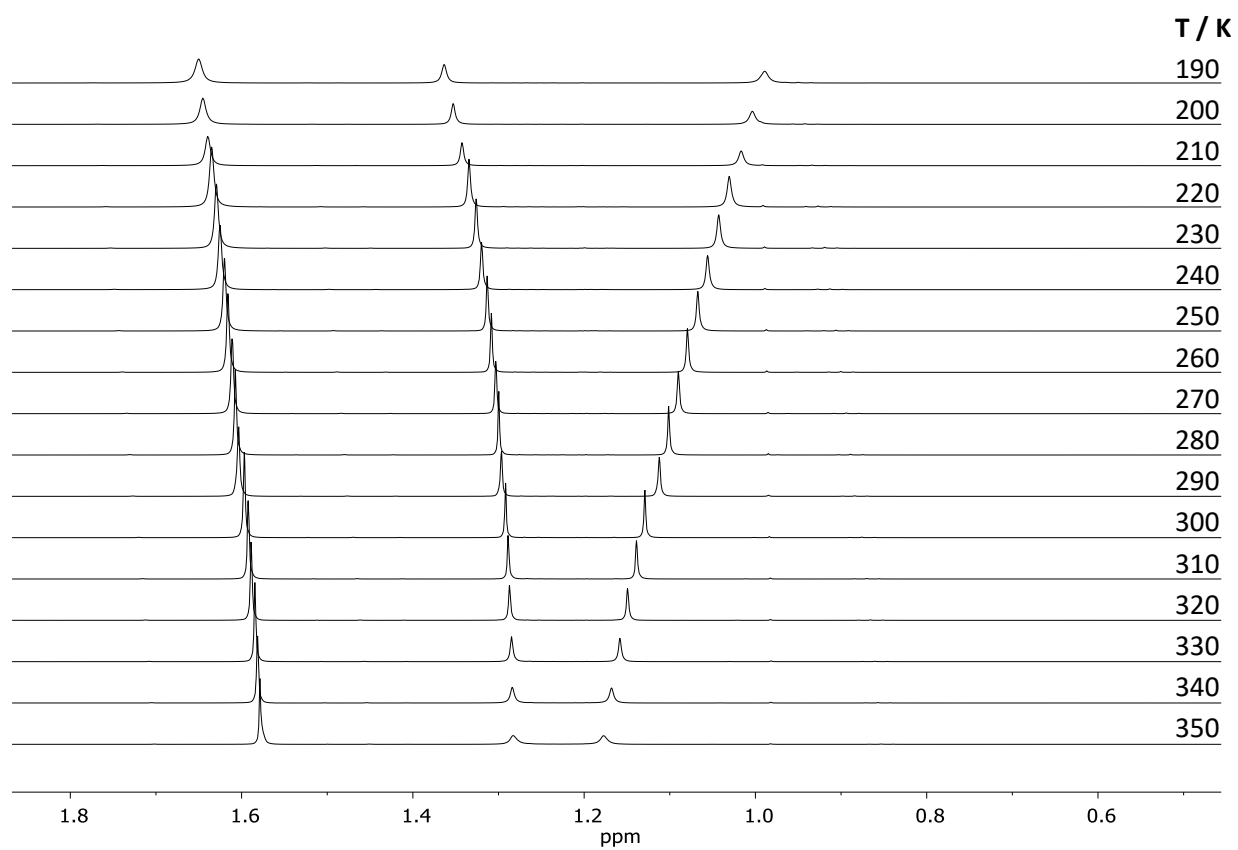


Figure S19. VT-¹H NMR spectrum of **3** (500 MHz, toluene-*d*⁸).

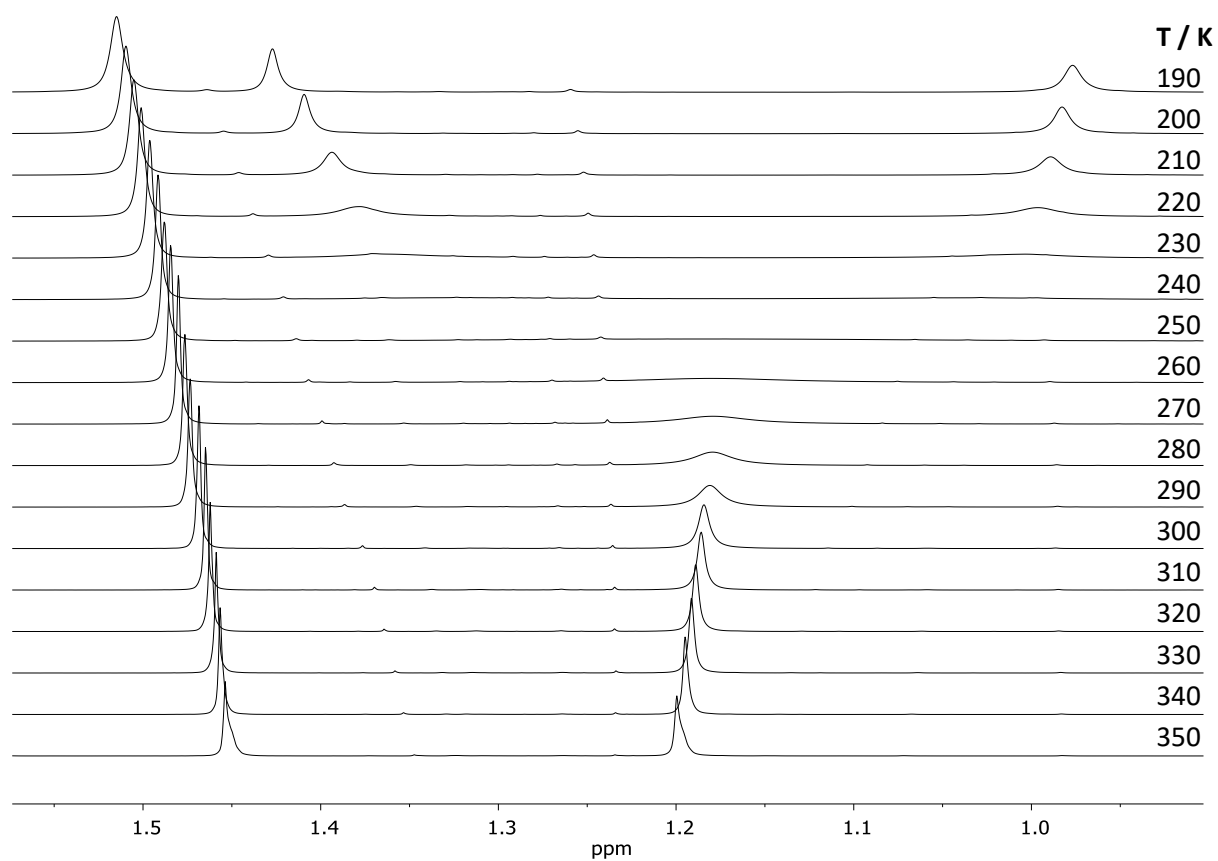


Figure S20. VT-¹H NMR spectrum of **4** (500 MHz, toluene-*d*⁸).

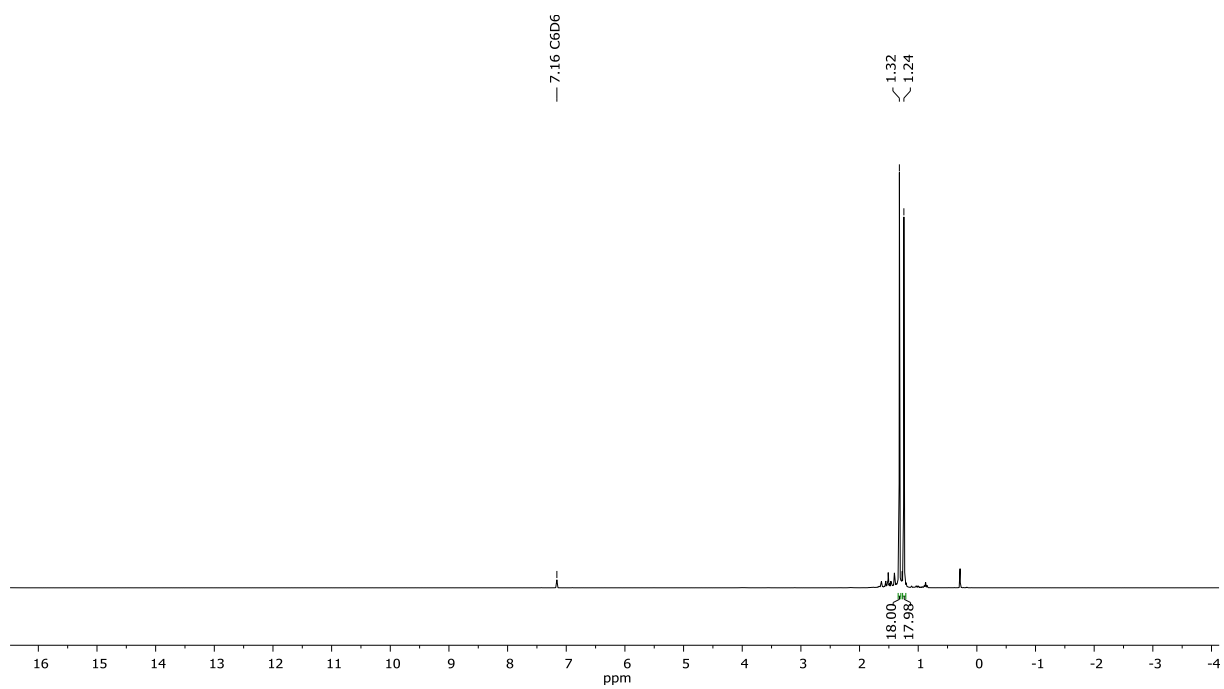


Figure S21. ^1H NMR spectrum of **1** (300 MHz, C_6D_6 , 300K).

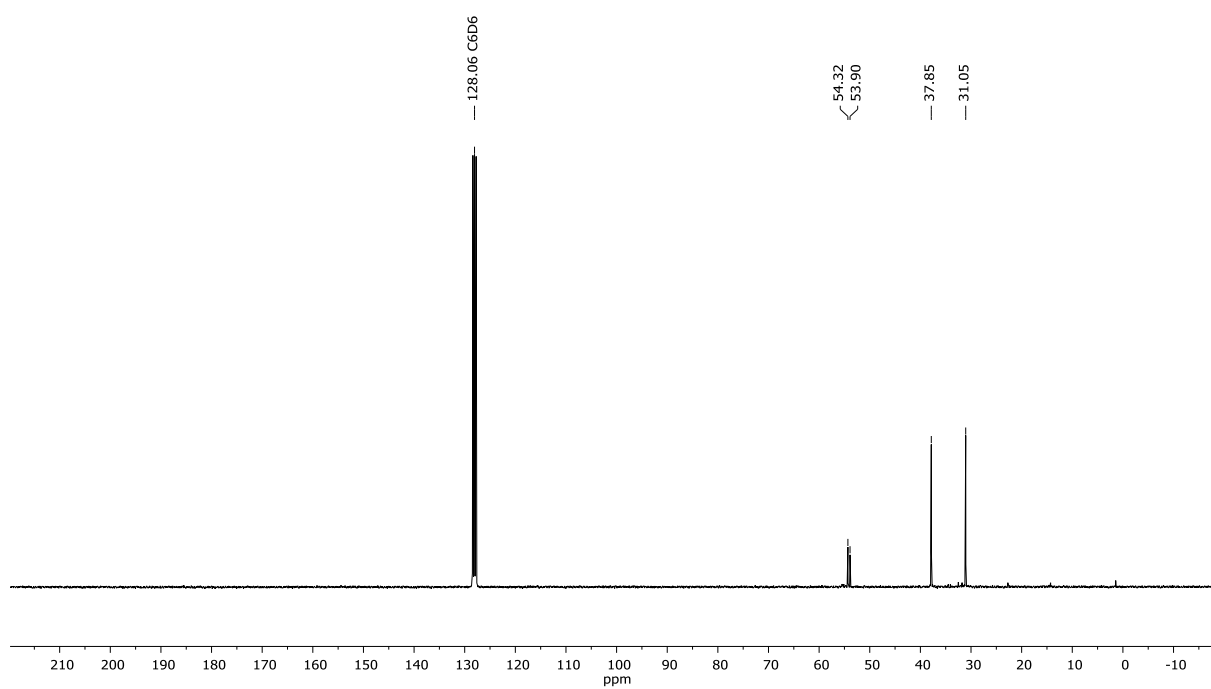


Figure S22. ^{13}C NMR spectrum of **1** (75.5 MHz, C_6D_6 , 300K).

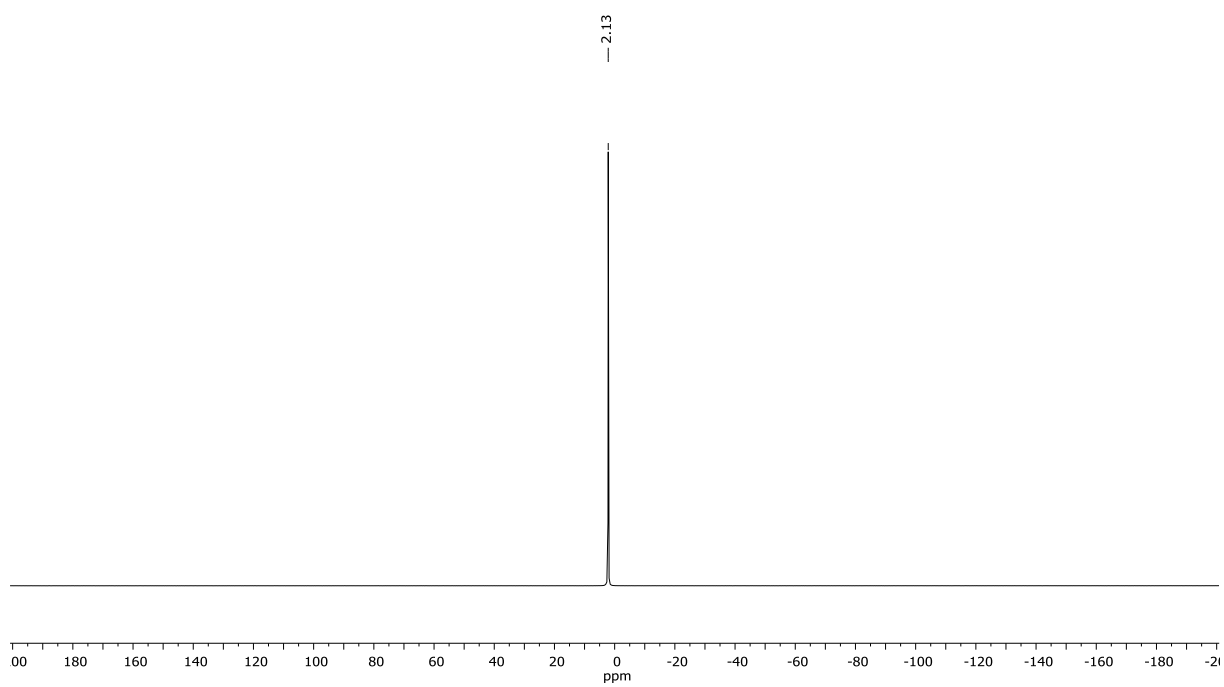


Figure S23. ^7Li NMR spectrum of **1** (117 MHz, C_6D_6 , 300K).

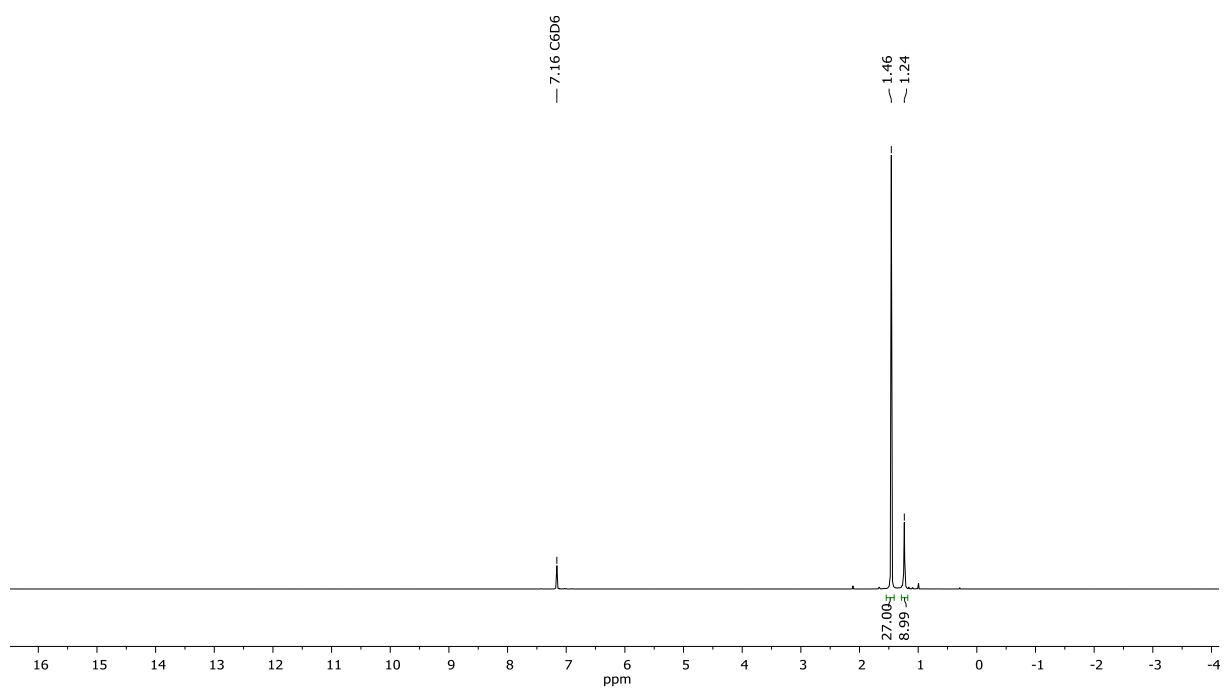


Figure S24. ^1H NMR spectrum of **2** (300 MHz, C_6D_6 , 300K).

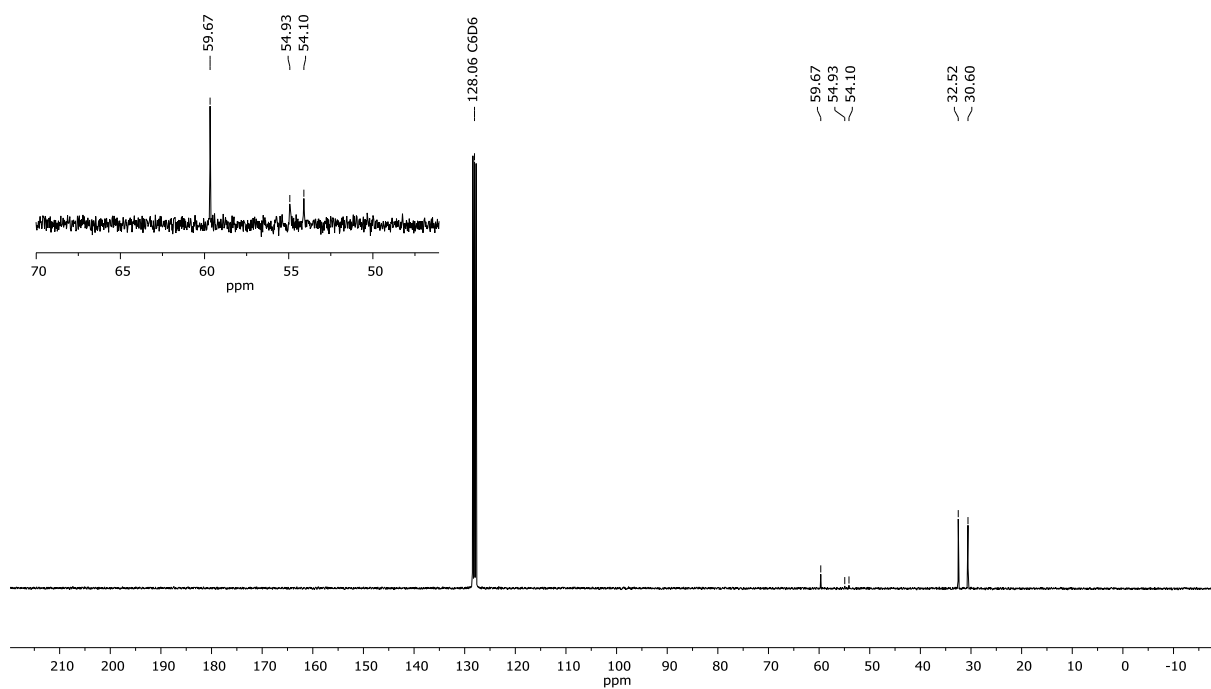


Figure S25. ^{13}C NMR spectrum of **2** (75.5 MHz, C_6D_6 , 300K).

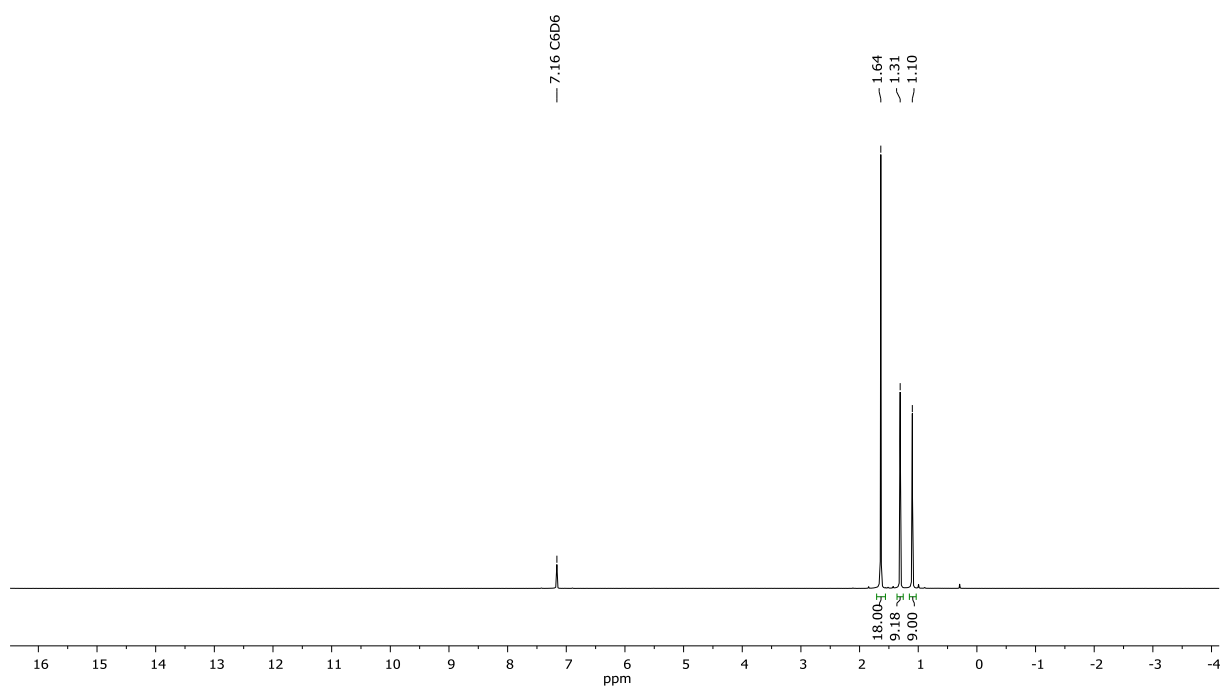


Figure S26. ^1H NMR spectrum of **3** (300 MHz, C_6D_6 , 300K).

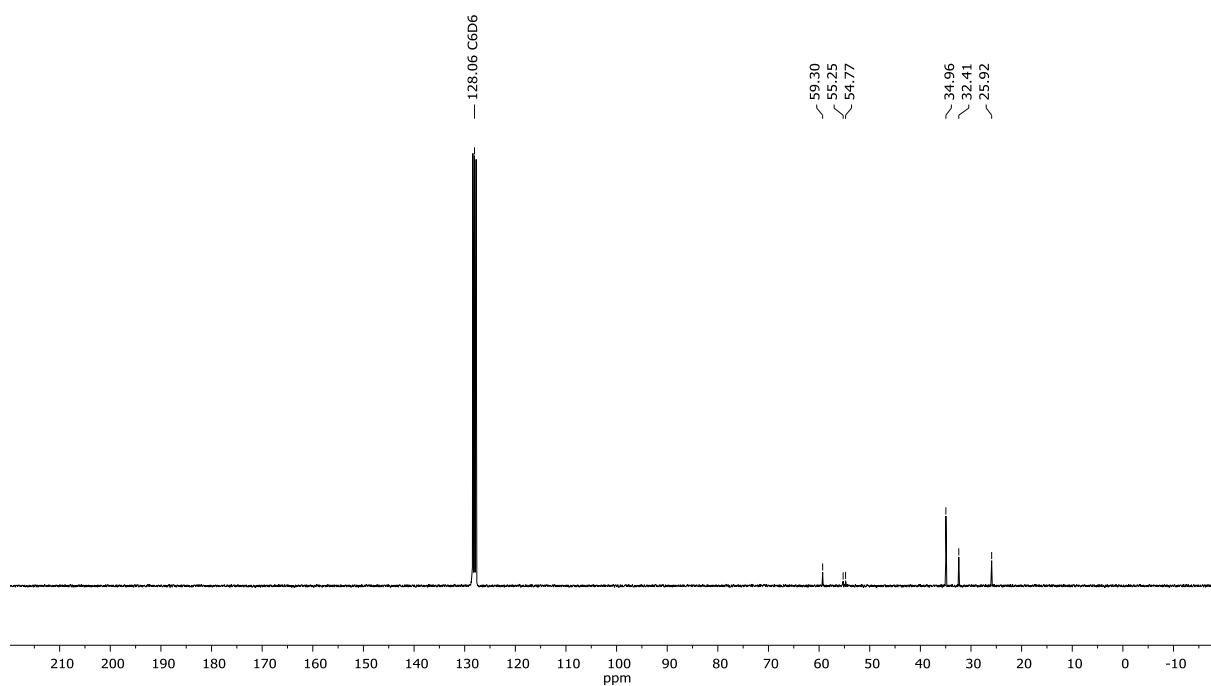


Figure S27. ¹³C NMR spectrum of **3** (75.5 MHz, C₆D₆, 300K).

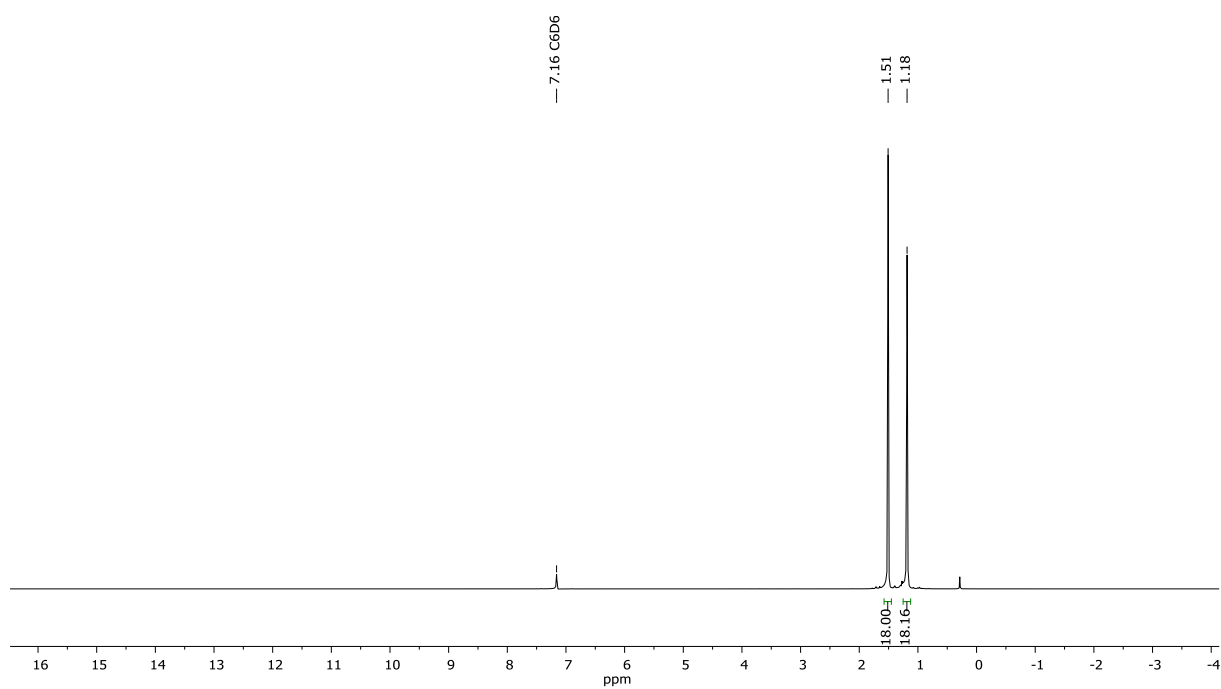


Figure S28. ¹H NMR spectrum of **4** (300 MHz, C₆D₆, 300K).

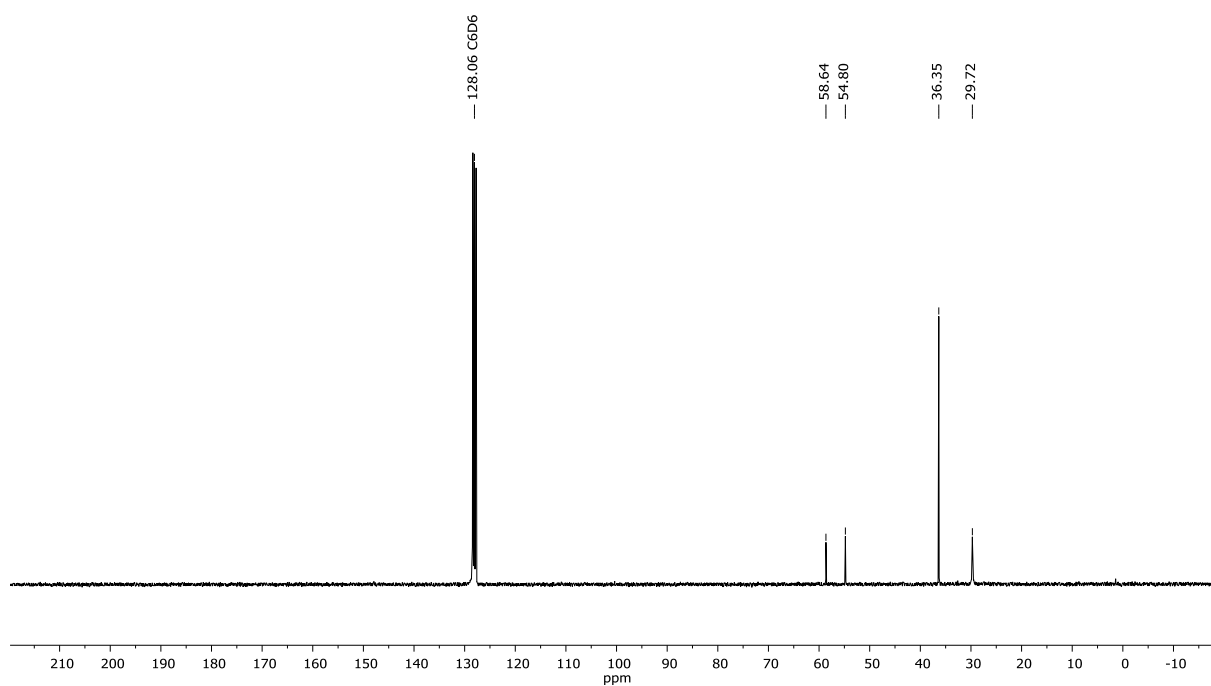


Figure S29. ¹³C NMR spectrum of **4** (75.5 MHz, C₆D₆, 300K).

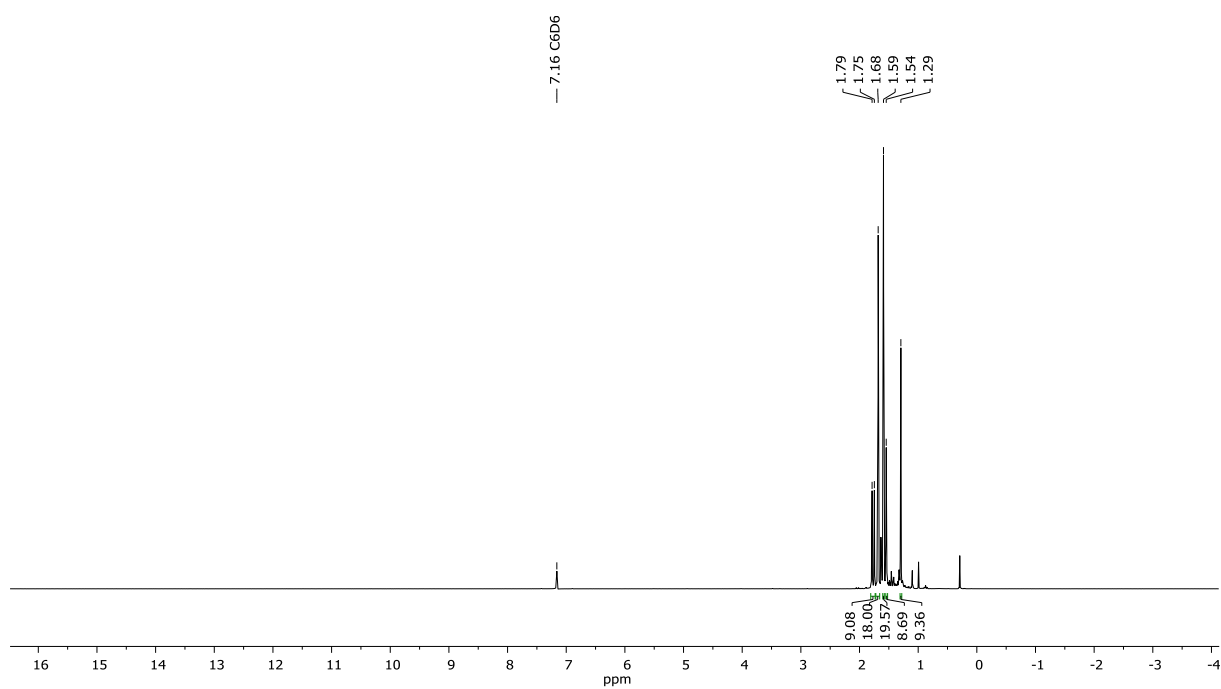


Figure S30. ¹H NMR spectrum of **6** (300 MHz, C₆D₆, 300K).

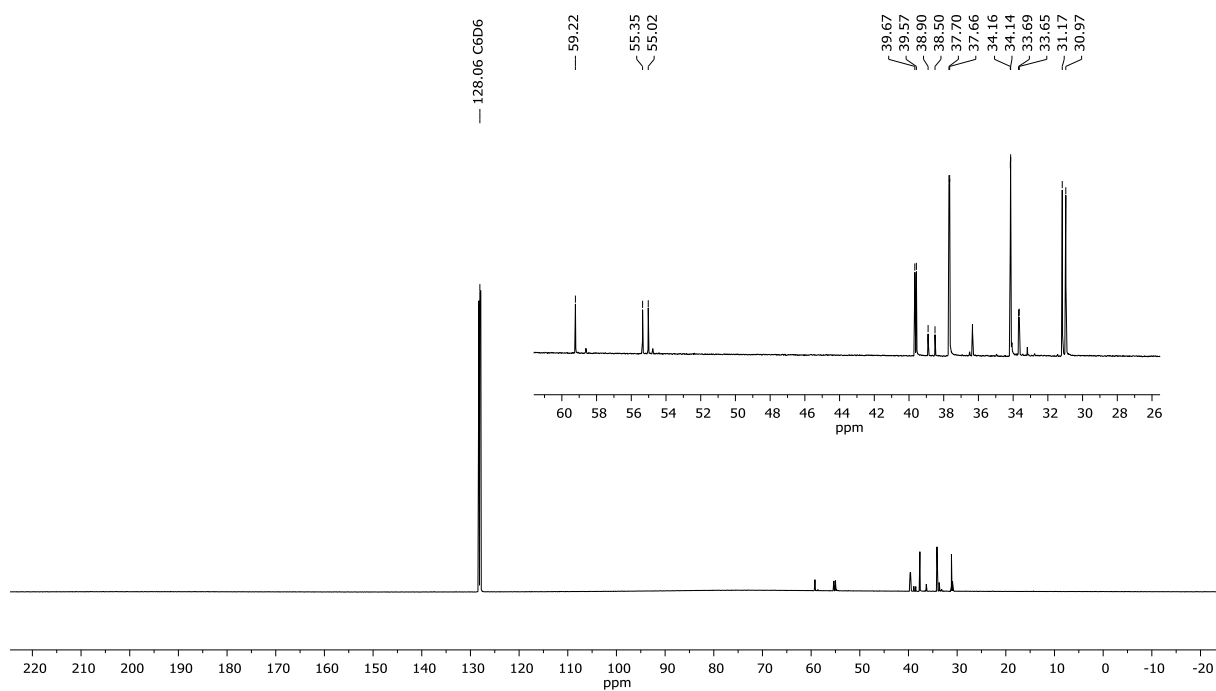


Figure S31. ^{13}C NMR spectrum of **6** (75.5 MHz, C_6D_6 , 300K).

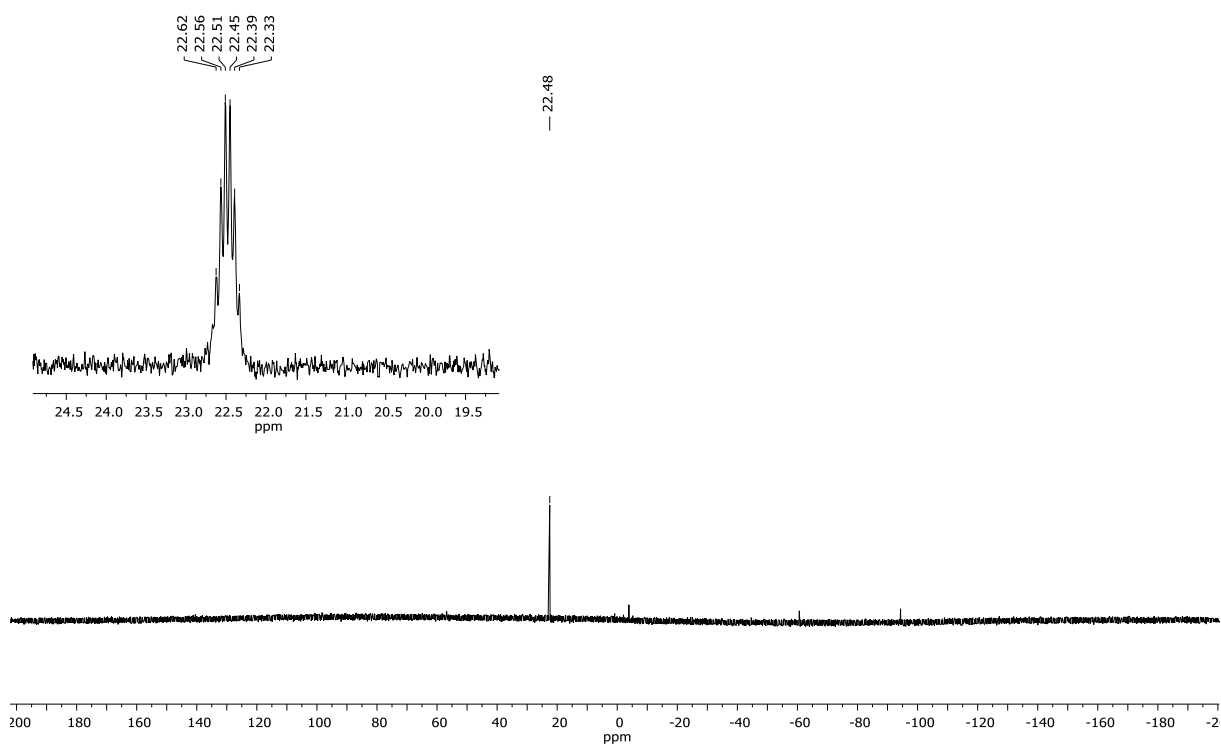


Figure S32. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and ^{31}P NMR spectrum (expansion) of **6** (101 MHz, C_6D_6 , 300K).

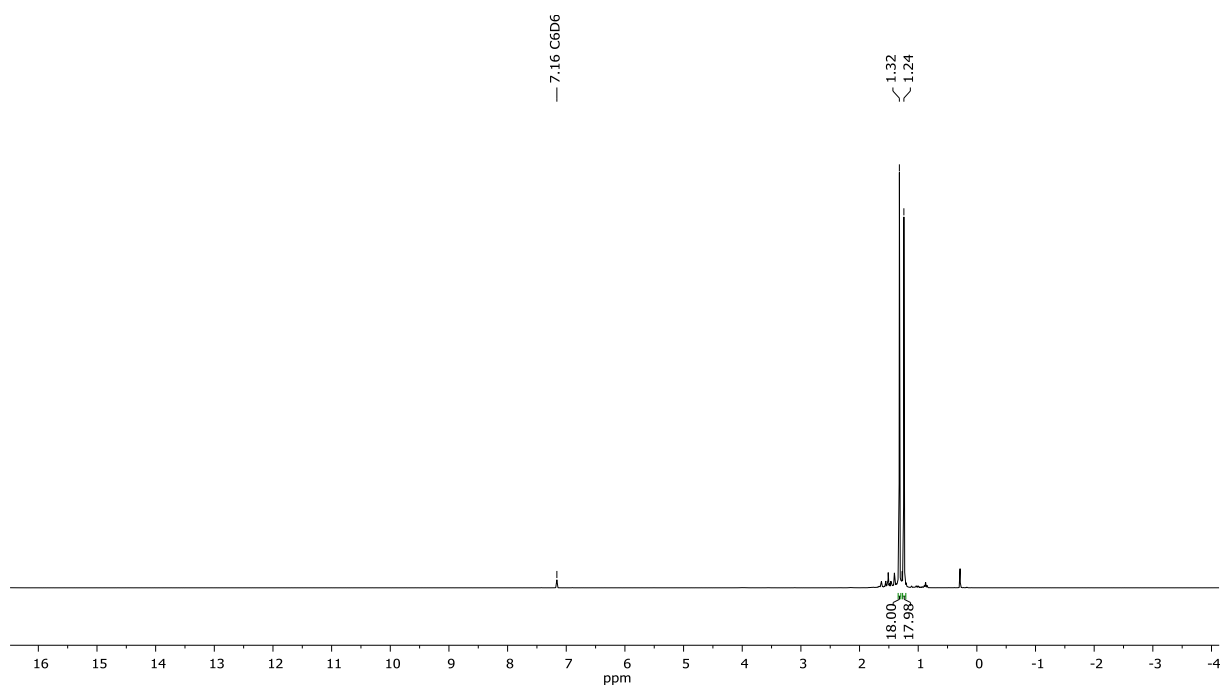


Figure S33. ^1H NMR spectrum of **7** (300 MHz, C_6D_6 , 300K).

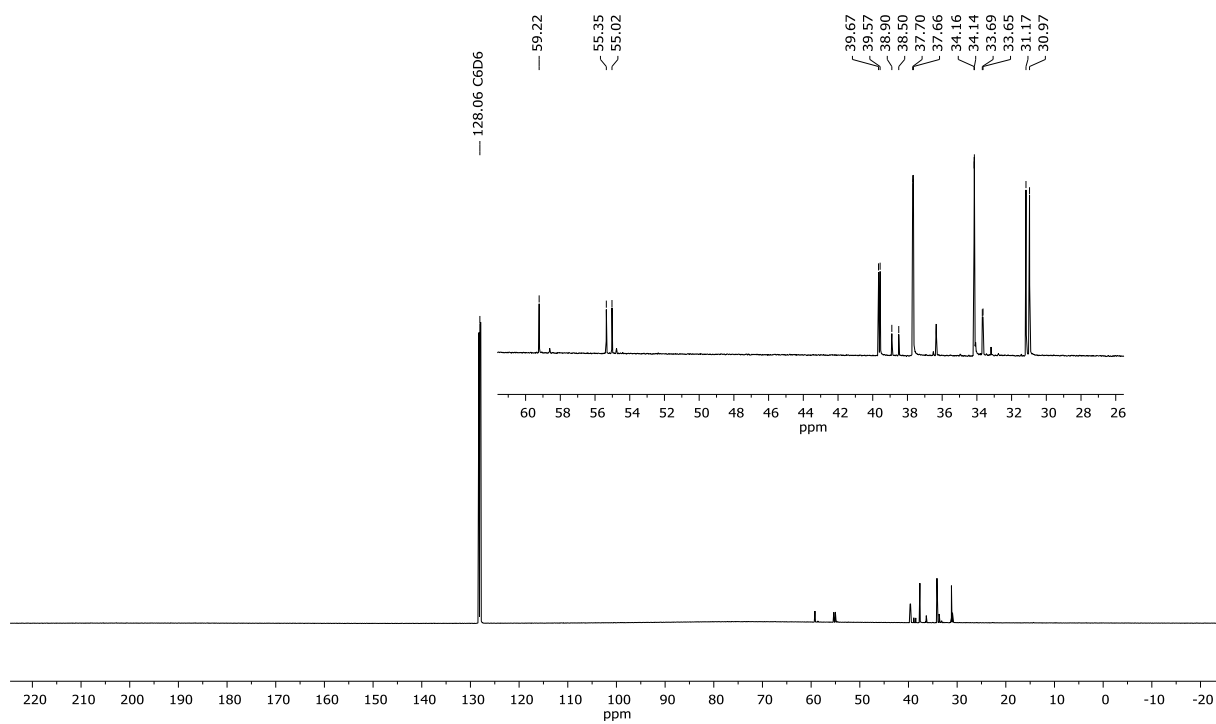


Figure S34. ^{13}C NMR spectrum of **7** (75.5 MHz, C_6D_6 , 300K).

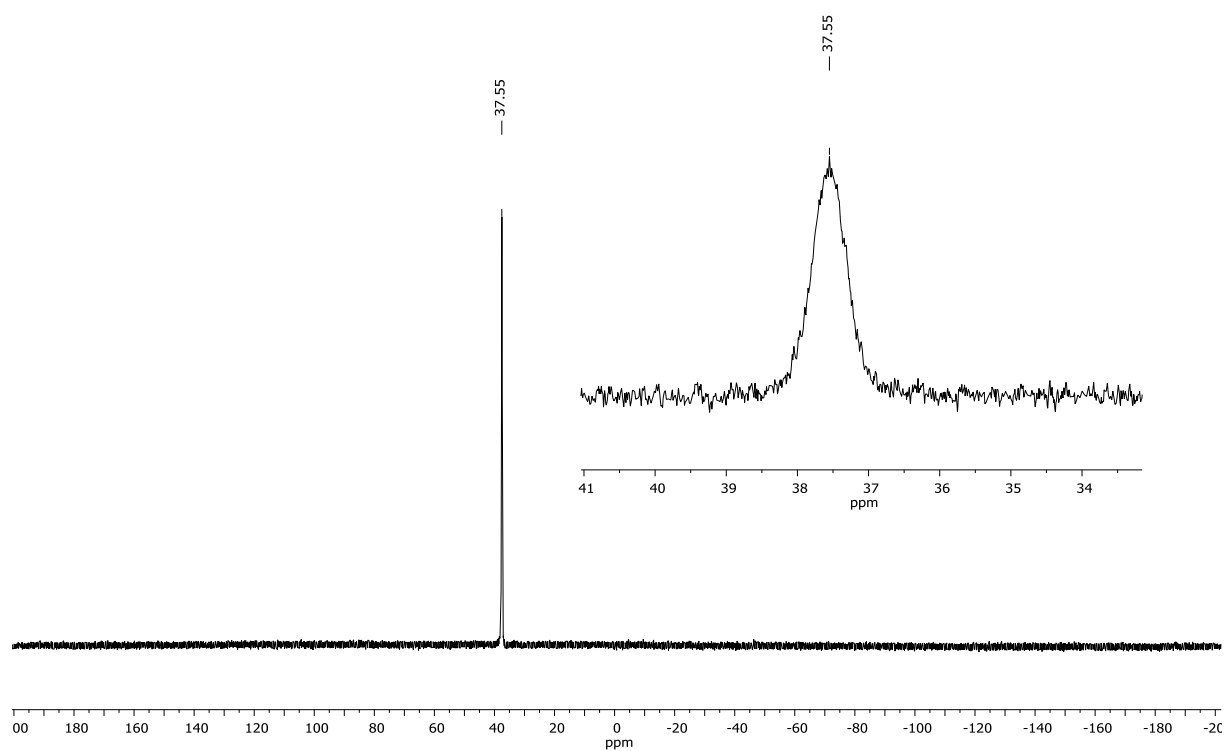


Figure S35. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and ^{31}P NMR spectrum (expansion) of **7** (101 MHz, C_6D_6 , 300K).

7 References

- [1] W. L. F. Armarego, C. L. L. Chai, in *Purif. Lab. Chem.*, Elsevier, **2003**, pp. 80–388.
- [2] B. Ringler, M. Müller, C. von Hänisch, *Eur. J. Inorg. Chem.* **2018**, 640–646.
- [3] H.-J. Vetter, H. Nöth, W. Jahn, *Z. Anorg. Allg. Chem.* **1964**, 328, 144–153.
- [4] M. Veith, A. Rammo, M. Hans, *Phosphorus. Sulfur. Silicon Relat. Elem.* **1994**, 93, 197–200.
- [5] G. M. Sheldrick, *Acta Cryst. C.* **2015**, 71, 3–8.
- [6] G. M. Sheldrick, *Acta Cryst. A.* **2015**, 71, 3–8.
- [7] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, 42, 339–341.